

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 796 871 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
24.09.1997 Bulletin 1997/39

(51) Int. Cl. 6: C08F 4/48, C08F 36/04,  
C08F 2/38

(21) Application number: 97200791.8

(22) Date of filing: 17.03.1997

(84) Designated Contracting States:  
BE DE ES FR GB IT NL  
Designated Extension States:  
RO

(30) Priority: 18.03.1996 US 13549

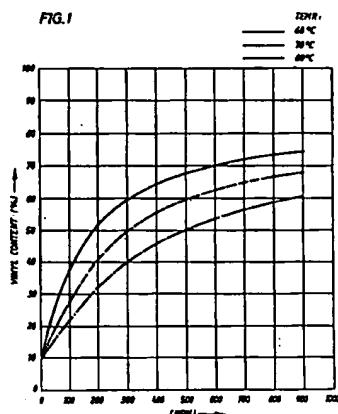
(71) Applicant: SHELL INTERNATIONALE RESEARCH  
MAATSCHAPPIJ B.V.  
2596 HR Den Haag (NL)

(72) Inventors:

- Bean, Arthur Robinson, Jr.  
Houston, Texas 77070 (US)
- Graafland, Teunis  
1031 CM Amsterdam (NL)

(54) Process for the polymerisation of conjugated diene monomers

(57) The invention provides a process for the polymerisation of conjugated diene monomers which comprises anionically polymerising the monomers in the presence of an anionic polymerisation initiator and a microstructure control agent for controlling the vinyl content of the polymer so obtained, whereby the control agent is added to the polymerisation mixture in two or more doses, or continuously.



## Description

The present invention relates to the anionic polymerisation of conjugated diene monomers in the presence of an anionic polymerisation initiator and a microstructure control agent for controlling the vinyl content of the polymer so obtained.

Polymers of conjugated dienes have been produced by numerous methods. However, anionic polymerisation of such dienes in the presence of an anionic polymerisation initiator is the most widely used commercial process. The polymerisation is carried out in an inert solvent such as hexane, cyclohexane or toluene and the polymerisation initiator is commonly an organo alkali metal compound, especially an alkyl lithium compound.

Microstructure control of conjugated diene polymers or conjugated diene polymer blocks within polymers is important because a controlled degree of branching in the polymer is desirable. If, such as in the case of butadiene, the diene in the polymer is all straight chain, such as 1,4-polybutadiene, the polymer when hydrogenated will be polyethylene and have crystallinity. In order to achieve good thermoplastic elastomeric properties in the polymer, it is desirable that the microstructure include a uniform specific degree of branching or vinyl content, such as 1,2-butadiene possesses. This will ensure that the desired glass transition temperature ( $T_g$ ) and hardness are achieved.

The desired control of the microstructure to include a desired amount of branching or vinyl content is commonly effected by including a microstructure control agent in the polymerisation mixture (i.e. the mixture comprising the conjugated diene monomers, the inert solvent, the anionic polymerisation initiator and polymer obtained). The desired level of vinyl content is achieved by properly selecting the type and the amount of these microstructure control agents, which are commonly Lewis basic compounds. Such compounds include ether compounds and tertiary amines. Suitable examples are cyclic ethers such as tetrahydrofuran, tetrahydropyran and 1,4-dioxane; aliphatic monoethers such as diethyl ether and dibutyl ether; aliphatic polyethers such as ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, diethylene glycol diethyl ether and diethylene glycol dibutyl ether; aromatic ethers such as diphenyl ether and anisole; tertiary amine compounds such as triethyl amine, tripropyl amine, tributyl amine; and other compounds such as N,N,N',N'-tetramethylethylene diamine, N,N-diethyl aniline, pyridine and quinoline.

Many of these microstructure control agents are temperature sensitive. In other words, they will produce varying amounts of vinyl content in the conjugated diene polymer at different temperatures. Thus, if a constant vinyl content is required in the conjugated polymer, the polymerisation must be carried out isothermally. Diethyl ether is often used because it is not as temperature sensitive as the others and does not require isothermal operation. Diethyl ether, however, has disadvantages. It is not as effective in producing conjugated diene polymer with a high vinyl content as other ethers and larger amounts of it have to be used. In fact, the amounts which are necessary require that it be separated from the main solvent, such as cyclohexane, in the case of a block polymerisation with, for example, styrene, whose polymerisation must be ether-free because ether kills too many of the styrene polymer chains. Separation of the diethyl ether is an additional step which increases the cost since it has to be purified and stored for reuse. Further, diethyl ether only allows up to approximately 38% vinyl content in butadiene polymers or butadiene polymer blocks. For some applications, however, it may be desired to achieve a higher vinyl content. Another disadvantage of diethyl ether is that it cannot be separated from some solvents such as isopentane.

In view of the foregoing, it would be advantageous to utilize a process for microstructure control which does not have to be operated isothermally. Further, it would be an advantage to be able to utilize a microstructure control agent which does not have to be used in large amounts requiring separation from the main solvent and purification. It would also be advantageous to be able to vary the microstructure of the polymer produced during the polymerisation process. The present invention as described below provides such advantages.

The present invention constitutes an improvement over the known process wherein the conjugated dienes are anionically polymerised in the presence of an anionic polymerisation initiator and a microstructure control agent which is used for controlling the vinyl content of the polymer obtained. The improvement to this process comprises adding the control agent to the polymerisation mixture in two or more doses.

In a preferred embodiment of the present invention, the polymerisation is carried out in a first adiabatic stage and a second isothermal stage. The control agent is then added to the polymerisation mixture in two or more doses during the adiabatic stage in amounts and at times sufficient to maintain the desired vinyl content of the polymer relatively constant. In another suitable embodiment of the present invention, the control agent is added in amounts and at times such that conjugated diene blocks with substantially different vinyl contents are produced in the polymer. The preferred microstructure control agents for use in the present process are 1,2-diethoxy-ethane and 1,2-diethoxy-propane.

In Fig. 1 a plot is shown of the temperature/vinyl content relationship for butadiene-styrene block copolymers which were made by using 1,2-diethoxy propane.

In Fig. 2 a plot is shown of vinyl content versus butadiene conversion for a conventional one step process.

In Fig. 3 a similar plot is shown for a three step addition process.

In accordance with the present invention polymers containing both ethylenic and/or aromatic unsaturation can be prepared by copolymerising one or more polyolefins, particularly conjugated diene monomers, by themselves or with one or more alkenyl aromatic hydrocarbon monomers. The polymers may, of course, be random, tapered, block or a

combination of these, as well as linear, star or radial.

- These polymers containing ethylenic unsaturation or both aromatic and ethylenic unsaturation may be prepared using anionic initiators or polymerisation catalysts, and bulk, solution or emulsion techniques. In any case, the polymer containing at least ethylenic unsaturation will, generally, be recovered as a solid such as a crumb, a powder, a pellet or the like. Polymers containing ethylenic unsaturation and polymers containing both aromatic and ethylenic unsaturation are, of course, available commercially from several suppliers.

When solution anionic techniques are used, conjugated diene polymers and copolymers of conjugated diene and alkenyl aromatic hydrocarbons can be prepared by contacting the monomer or monomers to be polymerised simultaneously or sequentially with an anionic polymerisation initiator such as Group IA metals, their alkyls, amides, silanolates, naphthalides, biphenyls and anthracenyl derivatives. Suitably, use is made of an organoalkali metal compound in a suitable solvent at a temperature within the range from -150°C to 300°C, preferably at a temperature within the range from 0°C to 100°C. Particularly effective anionic polymerisation initiators are organolithium compounds having the general formula:

15



Wherein:

R is an aliphatic, cycloaliphatic, aromatic or alkyl-substituted aromatic hydrocarbon radical having from 1 to 20 carbon atoms; and n is an integer of 1 to 4.

The conjugated diene monomers to be polymerised may be a mixture of two or more different conjugated diene monomers. Suitably, use is made of one type of conjugated diene. Conjugated dienes which may be polymerised anionically include those conjugated dienes containing from 4 to 12 carbon atoms such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, and 4,5-diethyl-1,3-octadiene. Conjugated diolefins containing from 4 to 8 carbon atoms are preferred. Alkenyl aromatic hydrocarbons which may be copolymerised include vinyl aryl compounds such as styrene, various alkyl-substituted styrenes, alkoxy-substituted styrenes, 2-vinyl pyridine, 4-vinyl pyridine, vinyl naphthalene, and alkyl-substituted vinyl naphthalenes.

Any of the solvents known in the prior art to be useful in the preparation of such polymers may be used. Suitable solvents include straight- and branched-chain hydrocarbons such as pentane, hexane, heptane, and octane, as well as, alkyl-substituted derivatives thereof; cycloaliphatic hydrocarbons such as cyclopentane, cyclohexane, and cycloheptane, as well as, alkyl-substituted derivatives thereof; aromatic and alkyl-substituted derivatives thereof; aromatic and alkyl-substituted aromatic hydrocarbons such as benzene, naphthalene, toluene, and xylene; hydrogenated aromatic hydrocarbons such as tetralin, and decalin; linear and cyclic ethers such as methyl ether, methyl ethyl ether, diethyl ether, and tetrahydrofuran.

Conjugated diene polymers and conjugated diene-alkenyl aromatic copolymers which can be prepared in accordance with the present invention include those copolymers described in U.S. Patents Nos. 3,135,716; 3,150,209; 3,496,154; 3,498,960; 4,145,298 and 4,238,202, which documents are hereby incorporated by reference. Conjugated diolefin-alkenyl aromatic hydrocarbon copolymers which may be prepared in accordance with the present invention also include the block copolymers as described in U.S. Patent Nos. 3,231,635; 3,265,765 and 3,322,856, which documents are also incorporated hereby by reference. Polymers which may be prepared in accordance with this invention also include coupled and radial block copolymers such as those described in U.S. Patent Nos. 4,033,888; 4,077,893; 4,141,847; 4,391,949 and 4,444,953, which documents are also incorporated hereby by reference. The radial polymers may be symmetric or asymmetric polymers.

As indicated herein above, it is common practice to control the microstructure of the diene polymer, i.e. the vinyl content (the 1,2-content in the case of polybutadiene), by adding to the polymerisation mixture a microstructure control agent. These are usually Lewis base compounds. They are conventionally added in one dose to the polymerisation mixture and the total vinyl content of the polymer is controlled by adjusting the ratio of the microstructure control agent and the polymerisation initiator and/or the polymerisation temperature.

Before the process of the present invention is carried out, the desired final vinyl content of the polymer must be chosen and the temperature profile of the reaction must be determined. The temperature is determined by the temperature of the feed and the total heat release during the reaction. Next, the temperature/vinyl content/concentration relationship for the desired control agent is utilized. This is determined by reacting the monomers with the control agent at different temperatures and measuring the vinyl contents. These data can be plotted as shown in Fig. 1.

The data are used to determine how much control agent is to be added to keep the vinyl content constant at different temperatures as the temperature increases. The control agent can be added in two or more doses at different temperatures. Continuous addition is the most preferred technique to give the closest possible control of the vinyl content. For expediency we approximate continuous addition with a series of doses. The number of doses depends on the total temperature change. More doses are required for greater temperature increases. The starting temperature indicates

the initial concentration and more will be needed as the temperature rises in the adiabatic portion of the reaction according to the pre-determined temperature profile.

Many microstructure control agents can be used in the process of the present invention. These include the aforementioned compounds and heavy ethers which are difficult to use in the present practice because they are temperature sensitive. Such heavy ethers include 1,2-diethoxy-ethane, 1,2-diethoxy-propane, orthodimethoxybenzene, 1,2-di-n-butoxy-ethane, 1-t-butoxy-2-n-butoxy-ethane, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>O-n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>OCH<sub>3</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>OCH<sub>2</sub>CH<sub>3</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>O-t-C<sub>4</sub>H<sub>9</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>OCHCH<sub>3</sub>-O-i-C<sub>4</sub>H<sub>9</sub>. These control agents which are stronger and can be used in smaller amounts than the presently used diethyl ether and thus, do not require recovery, storage and treating facilities, making the overall process less expensive to operate. They can be separated from solvents like isopentane. In fact, it is preferred that from 100 ppm to 300 ppm of the microstructure control agent is used to achieve the desired vinyl content. This amount may be split equally between the different doses of the agent which are added to the polymerisation mixture or varying amounts may be added at various points as required or it may be added continuously.

As indicated hereinabove, many of these microstructure control agents are temperature sensitive. As the temperature goes up, they become less effective and the vinyl content in the polymer produced goes down. Adding more microstructure control agent to the polymerisation mixture as the temperature rises helps keep the microstructure the same, i.e. the vinyl content does not vary appreciably. If this can be achieved, then the process does not have to be run isothermally, a difficult state to achieve. For reproducibility and control in the polymerisation process it is much easier to start up the process and run the process wherein the startup portion of the process is carried out adiabatically and the rest of the process is carried out isothermally. Thus, the microstructure control agent is suitably added to the polymerisation mixture during the startup or adiabatic portion of the process to maintain constant microstructure during that time. Addition of microstructure control agent is normally not necessary during the second or isothermal stage of the process because under that condition, the microstructure should not change appreciably.

Another important advantage of the present process is that conjugated diene blocks of different vinyl contents can be produced within the same polymer. For instance, a first conjugated diene polymer block can be produced with a desired vinyl content by adding a certain amount of a microstructure control agent. As the polymerisation proceeds, a second amount of microstructure control agent can be added to the polymerisation mixture to produce a second conjugated diene block which has a higher vinyl content. Thus, the properties of the polymer can be varied along the length of the polymer as well as its propensity to react to add various functionalizing agents such as epoxy, hydroxyl, amines, and anhydrides to the polymer chain.

The invention will now be illustrated by means of the following Examples.

#### Examples

In the following experiments, styrene-butadiene-styrene block copolymers were prepared. The general polymerisation scheme for this polymer is shown in Table 1 below.

40

45

50

55

Table 1: Dioxo Recipe

Below the recipe is given which served as base for the experiments described. Some values were adjusted during the course of the experiments (see Tables). Polymer: 12% solids; cy-C6/i-C5 75/25 w/w; 226.8 kg total.

Temp. 2nd step	Polymer 70°C
<u>Step I:</u>	
CH	(kg) 79.8
Total Sty	(kg) 4.5
BuLi	(mmole) 155
Reaction temp	(°C) 30-60
Reaction time	(min) 30
<u>Step II:</u>	
CH	(kg) 69.9
IP	(kg) 49.9
Dioxo	(g) 29.6
Bd rate	(kg/min) 0.456
Bd dosing time	(min) 40
Soak time	(min) 35
<u>Step III:</u>	
Temp	(°C) 60
Total Sty	(kg) 4.5
Sty dosing time	(min) 4
Soak time	(approx;min) 10

Cy-C6 = Cyclohexane = CH  
 i-C5 = isopentane = IP  
 dioxo = 1,2-diethoxy ethane  
 Bd = butadiene  
 Sty = styrene  
 Bu Li = butyl lithium

The step II and III polymerisations were carried out in a cyclohexane/isopentane mixture. Part of the butadiene was added batch-wise and the titration of the solvent was carried out by heat detection. The microstructure control agent, 1,2-diethoxy-ethane, was added after completion of the titration. After step I and during step II, samples were taken every 5 to 10 minutes to determine the molecular weight buildup (by gel permeation chromatography) and to determine the vinyl and styrene contents (by  $^1\text{H}$  NMR).

The polymer so obtained was hydrogenated. The hydrogenation was carried out using a nickel octoate/triethyl aluminium catalyst. After hydrogenation, the polymer cement was acid washed and neutralized. The mixing time was 30 minutes and the phases were allowed to separate for 15 minutes. The pH of the water phase was 10. The polymer was

then recovered by steam coagulation.

Run 4055 was carried out with semi-adiabatic temperature profile during step II, polymerising 50% of the butadiene batch-wise. Commencing at 30°C, the temperature was allowed to rise to 70°C without cooling. Then cooling was started in order to maintain the temperature at 70°C while adding the rest of the butadiene. The amount of microstructure control agent used was 130 ppm. In Run 4056, only 25% of the butadiene was polymerised batch-wise according to a semi-adiabatic temperature profile. In this case, the microstructure control agent was charged in three steps in order to compensate for the temperature gradient. At the beginning of step II, 55 parts per million was charged at 40°C, followed by 40 parts per million at 55°C and the final 35 parts per million at 70°C.

The polymerisation process data is shown below in Table 2:

10

Table 2

Polymerisation Process Data			
Run no.		4055	4056
15	Step I:		
20	Reaction time (min)	29	30
25	Transfer Temp (°C)	46	55
30	Step II:		
35	Temp. (°C)	30-70	40-70
40	Titration (ml)	15	12
45	Dioxo (ppm)	130	55/40/35
50	Batch Bd (kg)	11.41	5.71
55	Bd rate (kg/min)	0.59	0.59
60	Total Bd (kg)	22.82	22.82
65	Soak time (min)	30	30
70	Step III:		
75	Temp. (°C)	70-74	70-74
80	Soak time (min)	10	10
85	Sty rate (kg/min)	1.41	1.41
90	Total Sty (kg)	5.60	5.60

The analytical data showing the results of the tests on the samples which were taken during and after the polymerisation are shown below in Table 3:

45

50

55

Table 3

Analytical Data			
Run no.		4055	4056
Step I:			
MW <sup>1</sup>	( $\times 10^{-3}$ )	29.0	27.3
Step II:			
MW <sup>1</sup>	( $\times 10^{-3}$ )	242.6	243.5
Vin cont	(%)	45.1	43.2
Sty cont	(%)	19.2	18.7
Step III:			
MW <sup>1</sup>	( $\times 10^{-3}$ )	275.9	277.3
Vin cont	(%)	45.0	43.0
Sty cont	(%)	32.7	32.0

1: Apparent MW

25 In both Figures 2 and 3, the solid line shows the instantaneous or immediate vinyl distribution and the dotted line shows the average vinyl content of the polymer produced up to a particular time. Figure 2 shows the effect of using one dose of the microstructure control agent in the partially adiabatic process described above. The figure plots the vinyl distribution in the butadiene midblock as a function of butadiene conversion. It can be seen that the vinyl content tapers from 75% to 40% and doesn't become uniform until 30% conversion (constant temperature point). This is due to the  
30 high temperature sensitivity of the microstructure control agent used.

In Run 4056, the temperature change was compensated for by adding the microstructure control agent in three steps as discussed above. These results are shown in Figure 3. The figure shows that the vinyl content became uniform at 5% conversion and was maintained even though the temperature increased.

It can be seen in Figure 2 that the vinyl distribution drops off drastically and is much lower than the average distribution. However, when the process of the present invention is used (Figure 3), it can be seen that the actual vinyl distribution can be controlled such that it is very close to the cumulative distribution. This is important because it confirms that the actual instantaneous vinyl content is remaining at the needed level and not dropping off with temperature.

The tensile properties of the polymers after they were hydrogenated were determined. These tensile properties are shown in the following Table 4:

40

45

50

55

Table 4

Stress-strain tensile and Shore A hardness values for hydrogenated and compounded polymers <sup>1</sup> .		
	Stress (psi)	
Elongation (%)	3966	4056
100	124	136
300	204	218
500	307	339
TB <sup>2</sup>	976	952
EB <sup>3</sup> (%)	950	900
Shore A Hardness	49	45

1: Average values

2. Tensile at break

3. Elongation at break.

25 Where #3966 represents the product resulting from the process using non-temperature sensitive modifier, diethyl ether; and #4056 represents the product from the process using temperature sensitive modifier, dioxo, but employs the technique embodied here to compensate for temperature variation.

30 The data in Table 4 show that the tensile properties of the two polymers are very similar. This means that several of the important product characteristics of products made according to the prior art process can be duplicated using the new and improved process which, in addition, produces a polymer with a highly uniform vinyl content which, past experience has taught, will produce a polymer with desired overall thermoplastic elastomeric properties especially  $T_g$ .

Table 5

Actual Measurement v. Predicted $T_g$					
Sample	PS %w	PE %w	PB %w	$T_g$ (predicted) °C	$T_g$ (measured) °C
4055	28.27	38.16	33.25	-46	-482±2
4056	30.59	40.14	29.07	-48	-471±1
4060	30.19	41.97	27.65	-49	-491±1

45 According to the Fox Equation, we predict the  $T_g$  of the mid-block for the three materials. There is only a three °C difference among the three materials. Our measurement results cover the predicted values, but the error bars of the instrument and the variations in sample preparation are not small enough to differentiate themselves.

### Claims

1. A process for the polymerisation of conjugated diene monomers which comprises anionically polymerising the monomers in the presence of an anionic polymerisation initiator and a microstructure control agent for controlling the vinyl content of the polymer so obtained, whereby the control agent is added to the polymerisation mixture in two or more doses, or continuously.
2. A process according to claim 1, wherein the polymerisation is carried out in a first adiabatic stage and a second isothermal stage wherein the control agent is added to the polymerisation mixture during the adiabatic stage in amounts and at times sufficient to maintain the vinyl content of the polymer relatively constant.

3. A process according to claim 1 or 2, wherein the control agent is selected from the group consisting of 1,2-diethoxyethane, 1,2-diethoxypropane, 1,2-di-n-butoxy-ethane, 1-t-butoxy-2-n-butoxy-ethane, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>O-n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>OCH<sub>3</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>OCHCH<sub>3</sub>OCH<sub>2</sub>CH<sub>3</sub>, n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>O-t-C<sub>4</sub>H<sub>9</sub> and n-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>OCHCH<sub>3</sub>-O-i-C<sub>4</sub>H<sub>9</sub>.
- 5           4. A process according to claim 3 wherein the control agent is 1,2-diethoxyethane or 1,2-diethoxypropane.
- 10          5. A process according to any one of claims 1-4, wherein the control agent is used in an amount of from 100 to 300 ppm.
- 15          6. A process according to any one of claims 1-5, wherein the control agent is added in amounts and at times such that diene blocks with substantially different vinyl contents are produced.
- 15          7. A process according to any one of claims 1-6, wherein the control agent is added to the polymerisation mixture continuously.

20

25

30

35

40

45

50

55

FIG. 1

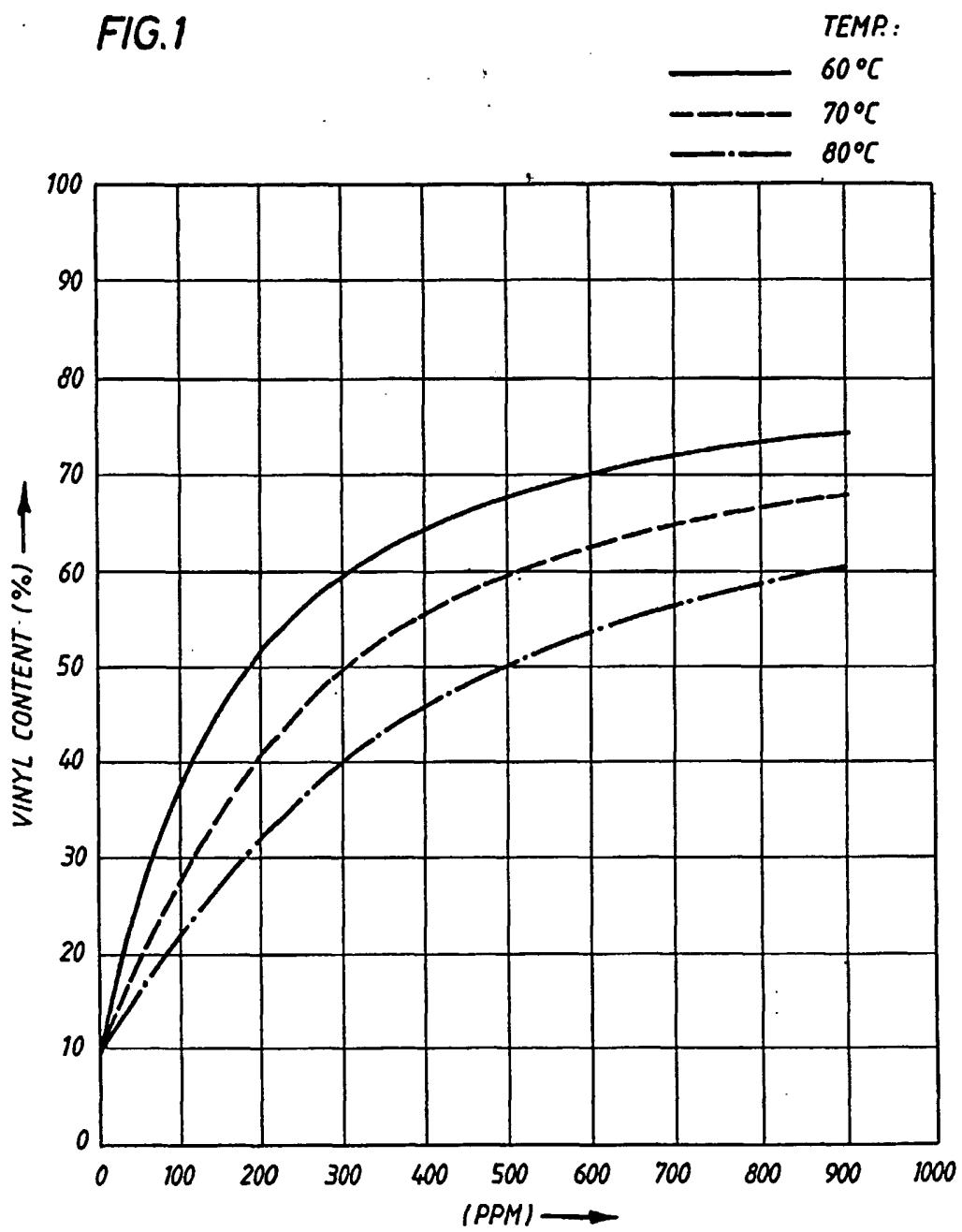


FIG. 2

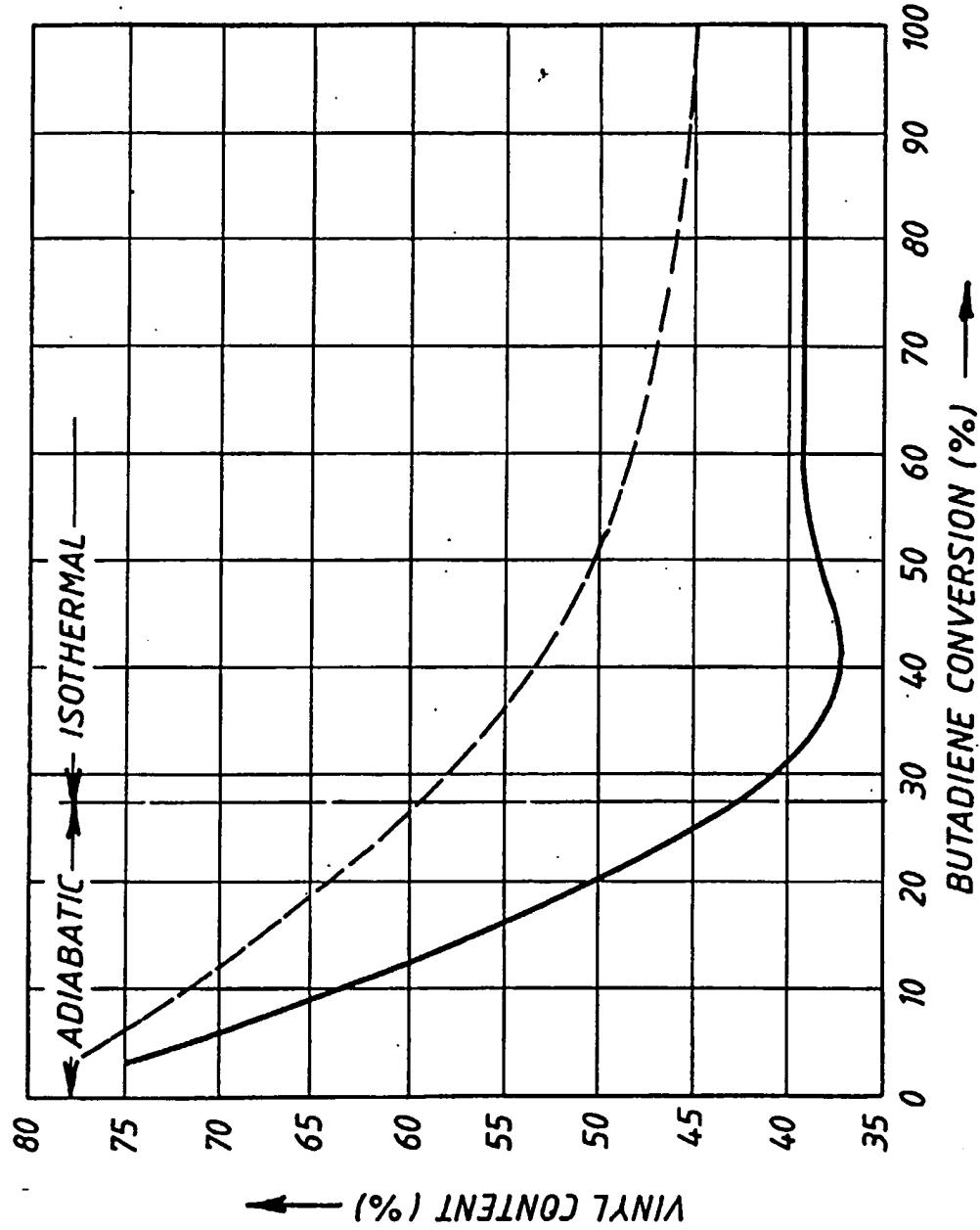


FIG. 3

